J3644

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : A23L 1/00, 1/0532, 1/0524, 1/0562, 1/24, A61K 7/48, 7/06 — A1

(11) International Publication Number: WO 95/12988

(43) International Publication Date: 18 May 1995 (18.05.95)

(21) International Application Number: PCT/EP94/03611

(22) International Filing Date: 2 November 1994 (02.11.94)

(30) Priority Data:
93308914.6 8 November 1993 (08.11.93) EP
(34) Countries for which the regional or international application was filed: AT et al.

(71) Applicant *(for all designated States except US)*: QUEST INTERNATIONAL B.V. [NL/NL]; Huizerstraatweg 28, NL-1411 GP Naarden (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: GIDLEY, Michael, John [GB/GB]; 45 Holmes Avenue, Raunds, Northants NN9 652 (GB). HEDGES, Nicholas, David [GB/GB]; 29 Southgate Drive, Towcester, Northamptonshire NN12 6JQ (GB).

(74) Agent: UNILEVER N.V.; Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).

Published
With international search report.

(54) Title: SUSPENSIONS OF GELLED BIOPOLYMERS

(57) Abstract

The invention relates to suspensions or dispersions of gelled and hydrated biopolymer particles as well as to a process for obtaining such suspensions, either from dried gelling biopolymers or from dissolved gelling biopolymers. Such suspensions may be used in food products (such as edible spreads and ice-creams) or personal care products (such as skin creams and moisturizers), e.g. to impart a fatty-like character to the product.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

SUSPENSIONS OF GELLED BIOPOLYMERS

The present invention relates to suspensions of gelled and hydrated biopolymer particles as well as to a process for obtaining such suspensions, either from dried gelling biopolymers or from dissolved gelling biopolymers.

It is widely known that gelled biopolymer particles having a specific size when dispersed or suspended in an aqueous medium may have useful properties such as imparting fat-like feel or character to products such as edible spreads and ice creams, but also to personal care products like skin creams and moisturizers. This is for example disclosed in EP 0 355 908 (A). Such biopolymer particles are prepared from the gels which are sheared, shredded or otherwise subjected to shear. In EP 0 501 758 (A) for example it is disclosed that a preformed gel is sheared or shredded. It is also possible to simultaneously form the gel phase and apply shear to the biopolymer, as is disclosed in EP 0 355 908 (A). A considerable disadvantage of these methods is that first a gel state has to be induced by cooling a solution containing said biopolymer, whereafter the gel is sheared either during its formation or following setting, under controlled circumstances to yield the desired particles.

Another disadvantage of these known methods for preparing a suspension of gelled biopolymers particles is that the preparation is carried out in a "wet" state, i.e. there is no active ingredient which can be isolated in a dry state (e.g. as a compact, dry powder or mix) which would be easy to store, handle, transport, sell, etcetera and which upon mixing with a (polar) liquid such as water directly yields the desired suspension or dispersion. The material according to EP-A-0 501 758 always contains from 72 to 99.9 percent water, which makes it a bulky material having considerable disadvantages on storage, transport, handling

etcetera.

Suspensions of gelled hydrated biopolymers can be used as fat replacers or fat simulating material to replace fat or oil partially or completely in food products. Another use for the suspensions is in products for personal care, like (skin-) moisturizers, skin creams, ointments, hair gels etcetera. For the purpose of this invention, such suspensions are hereinafter collectively referred to as a fat simulating material, although its application is not limited to food products but includes personal care products such as skin creams, moisturizers or hair gels.

In view of the disadvantages as set out above, there is a need for a convenient, easy to prepare fat simulating material obtainable without the need to first prepare a wet gel which thereafter needs to be sheared under controlled circumstances. Also, there is a need for such a material of which the active ingredient can be isolated in a dry state, thus yielding a compact, dry powder or mix which is ready to use conveniently at any time, and which, upon simple mixing with water or another polar solvent yields a fat simulating material.

It has now been found that these objectives above can be met by a suspension of particles, which particles comprise hydrated gelled biopolymers, which suspension is obtainable by hydrating dry particles of said biopolymers at a temperature of below T_{gel}, under the condition that dry particles are obtained by dehydrating at a temperature of equal to or above T_{gel} a solution comprising at least one biopolymer selected from the group consisting of agar, carrageenan, gelatin, gellan, furcelleran, alginate and (low methoxy) pectin. For the purpose of the invention, the term "hydrating" means: mixing of dry particles with a liquid to obtain completely wetted particles which are thereby swelled to the extent that individual particles can

still be identified (using suitable means, e.g. by microscopic observation) and that thus no complete dissolution of the particle material takes place. Due to swelling, an increase in mean size of preferably at least a factor 2 is obtained. Hydration is preferably carried out with a polar liquid, which preferably comprises water. More preferably, the suspended swelled particles thus obtained have a size which is between 2 and 30 times larger than their size in dry state.

For most purposes, it will be preferred that 80% by weight of the suspended biopolymer particles has a mean size below 100μm.

Biopolymers which can be used to prepare the suspensions according to the invention are selected from the group consisting of agar, carrageenan, gelatin, gellan, furcelleran, alginate, (low methoxy) pectin and mixtures comprising or or more of these biopolymers.

T_{gel} is herein to be understood as the temperature at which, upon cooling, an aqueous solution of the biopolymer concerned, sets to a gel. Of course a gel can only be formed under gelling conditions. Such gelling conditions may be different for the various biopolymers concerned but for each of them known in the art. For example, low methoxy pectin requires that a certain amount of calcium ions is present in the solution from which the gel is to be formed. Under normal conditions and using tap water, this may be the case without the addition of extra calcium ions. However, since the amount of calcium ions may influence T_{gel}, it may be desired for some purposes to increase or decrease the amount of calcium ions present in ways known in the art such as by adding sequestrants for removing Ca^{2+}. Similarly, carrageenan requires that a certain amount of metal ions like potassium, sodium and/or calcium ions are present in the aqueous solution in which the gel is to

be achieved. Therefore, potassium-, sodium- or other metal salt ions may be added intentionally in the form of a solution at any stage of the process of preparation of the gel.

Dry particles which can be used for the preparation of a suspension according to the invention may be obtained by dehydrating at a temperature of equal to or above T_{gel} a solution comprising at least one biopolymer selected from the group consisting of agar, carrageenan, gelatin, gellan, furcelleran, alginate and (low methoxy) pectin. Dehydration can be carried out in a number of ways known in the art, including roller drying and spray drying, but since it is needed that the biopolymer is obtained in a particulate form, a preferred way of drying is spray drying.

For specific purposes, it may be preferred to mix the dry particles comprising the biopolymers as defined above with an additional hydrocolloid (like e.g. xanthan, guar gum, locust bean gum or modified celluloses) and/or a starch-derivative (such as maltodextrin). This can be done by either simple mixing of the dry ingredients or by co-drying (e.g. co-spray-drying) a solution of the biopolymers with the additional compound.

An integrated process for the preparation of a suspension according to the invention, starting from a solution of at least one (gellable) biopolymer selected from the group consisting of agar, carrageenan (kappa- and iota-), gelatin, gellan, furcelleran, alginate and (low methoxy) pectin) may comprise the following steps:

a. drying the solution at a temperature of at least T_{gel}, followed by or simultaneously with
b. particulation of the dry material, followed by
c. hydrating the obtained particles with a polar liquid at a temperature lower than T_{gel}.

Preferably, step a. and b. are carried out simultaneously, which can be achieved by e.g. spray drying the solution comprising the biopolymer.

For preparing a fat simulating material any suitable biopolymer may be used depending on the specific application, as long as the biopolymers used are capable of forming a gel. Examples of such biopolymers are: carrageenan, gelatin, gellan, furcelleran, alginate, pectin or mixtures thereof. The specific application and the type of biopolymer may also determine the amount of particles needed to achieve the desired properties of a fat simulating material. Amounts may range up to 15% (by dry weight) of particles, calculated on the total amount of suspension.

Depending on the end-use of the suspensions according to the invention they may further comprise components like flavours, fragrances, colours, vitamins, salts, sugars, sugar alcohols, UV-absorbers, emulsifiers or other adjuncts.

The suspensions according to the invention may be used in a food product or personal care product, for example in order to partially or completely replace fat of animal or vegetable origin which would be normally present therein.

The suspensions according to the invention can be may be used to replace all or a portion of the fat, oil or cream in food products like ice cream, yoghurt, salad dressings, mayonnaise, cream, cream cheeses, other cheeses, sour cream, sauces, icings, whipped toppings, frozen confections, milk, coffee whiteners and spreads. The suspension according to the invention can also be used in personal care products.

The invention is illustrated by the following examples but

Table 1: particle size distribution dry agar particles (cumulative mean diameters)

upper limit (μm)	no. 1	no. 2	no. 3
5.0	22.28	29.57	29.25
7.5	59.69	68.78	65.73
10.0	82.28	87.85	81.81
12.5	92.35	95.46	90.68
15.0	96.79	98.20	94.50
17.5	98.70	99.26	97.27
20.0	99.60	99.63	98.67
22.5	99.84	99.83	99.48
25.0	99.98	99.88	99.86
27.5	100.00	100.00	100.00

Example 2:

The particles were dispersed or suspended in water in the following manner:

1. dried agar powder as obtained by spray drying according to the previous example (1 g) was gradually dispersed in cold water (100 ml) using an Ultraturrax T25 Homogeniser with a 16N probe (speed setting 8000 rpm).
2. Once the powder was fully dispersed the homogenisation speed was increased to 24000 rpm for 2-3 minutes.
3. The thus obtained particles were left to equilibrate for at least 1 hour before being measured. The obtained mix appeared to be translucent.

Image analysis on the resulting suspensions was not possible using the Quantimet, due to the similarity between the particle and solvent refractive indices. In order to determine the particle size of the dispersed particles a

is in no way limited thereto.

Example 1:

By co-spray drying at a temperature T above T_{gel} three samples of agar containing particles were prepared. The obtained particles contained the following ingredients:

no:	composition:	ratio (weight):
1	agar + maltodextrin	1 : 4
2	agar + maltodextrin + xanthan	1 : 3 : 0.05
3	agar + maltodextrin + xanthan	1 : 3 : 0.1

The agar used in all experiments was: Biogar (ex Quest International). The maltodextrin used in all experiments was: Paselli SA2 (ex Avebe). The xanthan used in all experiments was: Jungbunzlauer food-grade xanthan.

A conventional spray-drier was used having the following diameters: total chamber height is 1.8 meters, the top cylindrical section having a diameter of 1.3 meters and a height of 1.0 meters with the conical section being at an angle of 60° for 0.8 meters from the cylinder. Inlet temperature of the spray-drier was 190°C, outlet temperature about 90°C. Feed rate was 9 l. per hour. The agar concentration was about 3.5% by weight and does not include the other ingredients. A spinning disc-type atomizer was used for particulation.

The particle sizes of the dried powders were obtained using a Quantimet 970 Image Analyser. The powders were spread over a microscope slide which was sonicated in order to obtain, as best as possible, discrete particles. It should be noted that the image analysis routine in the Quantimet ignores large, irregular shaped particles in determining particles sizes, i.e. particles that have clumped together. The results of the obtained particle size measurements of the dry particles are set out in table 1.

Malvern Mastersizer X was employed. The results are set out in table 2.

Table 2: particle size distribution suspended agar particles (cumulative mean diameters)

upper limit (μm)	no. 1	no. 2	no. 3
5.24	0.03	0.0	0.0
7.78	0.33	0.08	0.11
11.55	1.69	1.51	1.42
17.15	9.82	11.16	9.93
25.46	31.57	34.03	30.91
37.79	65.44	62.80	59.11
56.09	90.85	84.16	81.32
83.26	97.79	93.24	91.14
123.59	97.81	96.22	94.66
183.44	98.14	98.27	97.45
272.31	99.37	99.69	99.49
404.21	100.00	100.00	100.00

Example 3:

Kappa-carrageenan particles were dispersed or suspended in water in the following manner:

1. dried kappa-carrageenan (ex Quest International, tradename Deltagel) powder as obtained by spray drying similarly to example 1 (1 g) was gradually dispersed in cold water (100 ml) containing 0.015M KCl using an Ultraturrax T25 Homogeniser with a 16N probe (speed setting 8000 rpm).
2. Once the powder was fully dispersed the homogenisation speed was increased to 24000 rpm for 2-3 minutes.
3. The thus obtained particles were left to equilibrate for at least 1 hour before being measured. The obtained mix appeared to be translucent.

In order to determine the particle size of the dispersed particles a Malvern Mastersizer X was employed. The results are set out in table 3.

Table 3: particle size distribution suspended carrageenan particles (cumulative mean diameters)

Upper limit μm	no. 4
15.58	0.32
22.97	8.04
33.87	35.08
49.95	67.54
73.66	89.47
108.61	97.70
160.17	98.84
286.82	98.84
513.61	98.91
1356.26	100.00

Example 4:

A moisturizing personal care product was prepared using the following formulation (all percentages by dry weight):

2.5% spray dried kappa-carrageenan (similar to the carrageenan obtained in example 3)
3% glycerol
0.06% colouring agent
0.1% flavour
0.1% preservative (sodium methylbenzoate)

0.11% potassium chloride
remainder water

i) All ingredients, excluding the carrageenan, were dissolved in the water at room temperature.
ii) The carrageenan was gradually added to the resulting liquid and suspended using an T25 ultraturrax with a 18G probe, on a low speed setting.
iii) Once the suspension is complete, it was mixed at a higher shear setting for about 2 minutes to achieve a smooth texture.

The resulting product was a pourable, smooth composition with a fatty-like appearance suitable for topical application to the skin.

Example 5:

A dressing type product was prepared using the following recipe (all percentages based on dry weight):

6% co-spray dried agar/maltodextrin/xanthan mixture
(ratio 1:3:0.05 respectively)
maltodextrin being a 2DE maltodextrin (Paselli SA2, ex Avebe)
xanthan being a food-grade xanthan ex Jungbunzlauer
4% sucrose
2.2% salt
2% flavours and spices
0.13% potassium sorbate (preservative)
remainder water

i) all ingredients were dissolved at room temperature, excluding the agar-containing mixture
ii) the solution was titrated to pH 3.8 with wine vinegar
iii) the agar-containing mixture was slowly added to the aqueous composition under moderate shear using an

ultraturrax T25 with 18G probe on a medium setting.

iv) once addition was complete, shear was increased to high setting for about 2 minutes.

A product was obtained which had a rheology and texture very much similar to conventional fat containing dressing type products. Furthermore, the product obtained showed good stability.

Example 6:

A similar product as in example 5 was prepared by using 7.5% co-spray dried agar/maltodextrin (ratio 1:4 respectively)

CLAIMS

1. A suspension of particles, which particles comprise hydrated gelled biopolymers, which suspension is obtainable by hydrating dry particles of said biopolymers at a temperature of below T_{gel}.

2. A suspension according to claim 1, characterized in that the dry particles are obtained by dehydrating at a temperature of above T_{gel} a solution comprising a biopolymer capable of forming a gel.

3. A suspension according to claim 1-2, characterized in that the biopolymer particles have a size which is between 2 and 30 times larger than in their unhydrated state.

4. A suspension according to claim 1-3, characterized in that at least 80% by weight of the hydrated biopolymer particles has a mean size below 100μm.

5. A suspension according to claim 1-4, characterized in that the biopolymer is selected from the group consisting of agar, carrageenan, gelatin, gellan, furcelleran, alginate, (low methoxy) pectin and mixtures thereof.

6. A suspension according to claim 1-5, characterized in that it further comprises a hydrocolloid and/or a starch based material.

7. A suspension according to claim 6, characterized in that the starch based material comprises maltodextrin.

8. A suspension according to claim 6, characterized in that hydrocolloid comprises xanthan, guar gum, locust bean gum or modified celluloses.

9. A suspension according to claim 1-8, characterized in that it further comprises flavours, fragrances, colours, vitamins, salts, sugars, sugar alcohols, emulsifiers or other water soluble adjuncts.

10. Food product or personal care product comprising a suspension according to claim 1-9.

11. Use in food products or personal care products of a suspension according to claim 1-9 to replace fat of animal or vegetable origin partially or completely.

12. A process for the preparation of a suspension comprising mixing dry particles which comprise a biopolymer capable of forming a gel, with a liquid at a temperature lower than T_{gel} of said biopolymer.

13. A process according to claim 12, characterized in that the polar liquid comprises water.

14. A process according to claim 12-13, characterized in that the biopolymer capable of forming a gel is selected from the group consisting of agar, carrageenan, gelatin, gellan, furcelleran, alginate, (low methoxy) pectin and mixtures thereof.

15. A process for the preparation of a suspension comprising:

a. drying at a temperature of at least T_{gel} an aqueous solution comprising a biopolymer selected from the group consisting of agar, carrageenan, gelatin, gellan, furcelleran, alginate, (low methoxy) pectin and mixtures thereof, followed by or simultaneously with

b. particulation of the dry material

c. hydrating the obtained particles with a polar liquid at a temperature lower than T_{gel}.

16. A process according to claim 15, characterized in that step a. and b. are carried out simultaneously.

17. A process according to claim 15-16, characterized in that step a. is carried out by spray drying the solution comprising the biopolymer.

INTERNATIONAL SEARCH REPORT

Interna l Application No
PCT/EP 94/03611

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23L1/00 A23L1/0532 A23L1/0524 A23L1/0562 A23L1/24
A61K7/48 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A23L A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 355 908 (UNILEVER) 28 February 1990 cited in the application ---	
A	EP,A,0 501 758 (HERCULES INCORPORATED) 2 September 1992 cited in the application ---	
A	DATABASE WPI Week 8340, Derwent Publications Ltd., London, GB; AN 83-779408 & JP,A,58 142 936 (MORINAGA) 25 August 1983 see abstract --- -/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
30 January 1995	13.02.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Meertens, J

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 8834, Derwent Publications Ltd., London, GB; AN 88-237971 & JP,A,3 169 948 (SANE) 13 July 1988 see abstract	
A	US,A,4 663 178 (CONAGRA) 5 May 1987	
A	DE,A,25 50 423 (AB FYRTORNET) 26 May 1976	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0355908	28-02-90	AU-B-	619333	23-01-92
		AU-A-	3997289	22-02-90
		JP-A-	2191540	27-07-90
EP-A-0501758	02-09-92	AU-A-	1123292	27-08-92
		CA-A-	2061498	27-08-92
		JP-A-	5003767	14-01-93
		US-A-	5324531	28-06-94
US-A-4663178	05-05-87	NONE		
DE-A-2550423	26-05-76	SE-B-	389796	22-11-76
		SE-B-	398592	09-01-78
		SE-A-	7414409	17-05-76
		SE-A-	7508415	24-01-77